

Correlation functions in ionic liquid at coexistence with ionic crystal. Results of the Brazovskii-type field theory*

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Abstract

Correlation functions in the restricted primitive model are calculated within a field-theoretic approach in the one-loop self-consistent Hartree approximation. The correlation functions exhibit damped oscillatory behavior as found before in the Gaussian approximation [Ciach et al., J. Chem. Phys. **118**, 3702 (2003)]. The fluctuation contribution leads to a renormalization of both the amplitude and the decay length of the correlation functions. The renormalized quantities show qualitatively different behavior than their mean-field (MF) counterparts. While the amplitude and the decay length both diverge in MF when the λ -line is approached, the renormalized quantities remain of order of unity in the same dimensionless units down to the coexistence with the ionic crystal. Along the line of the phase transition the decay length and the period of oscillations are independent of density, and their values in units of the diameter of the ions are $\alpha_0^{-1} \approx 1$ and $2\pi/\alpha_1 \approx 2.8$ respectively.

* Dedicated to Prof. R. Evans on the occasion of his 60th birthday

I. INTRODUCTION

Distribution of charges in ionic systems has been a subject of considerable interest for many years. In theoretical studies of systems such as molten salts, electrolytes or ionic liquids the interaction potential is often approximated by the restricted primitive model (RPM), where identical hard spheres carry positive or negative charges with equal magnitude. Earlier studies concentrated on correlation functions for charges in ion-dilute systems [1, 2, 3], and later the ion-dense systems were also investigated [2, 3, 4, 5, 6, 7, 8, 9]. However, the question of the form of the correlation functions in the liquid (fused salt) at the coexistence with the ionic crystal remain open. Whereas the correlation functions in a liquid can be quite accurately described within liquid theories such as the mean-spherical approximation (MSA) [3, 5], the transition to a crystalline phase is not predicted by the liquid theories. The liquid-solid transition in the RPM was determined within the density functional theory of freezing in Ref. [10], but the charge-charge correlation function is not discussed in this work. Both the phase transition and the correlation functions can be found on the same level of approximation within the framework of the field theory for the RPM introduced in Ref.[11]. In this work we calculate the correlation functions in the RPM by applying the Brazowskii-type approximation. We pay particular attention to the decay length, the period of damped oscillations and the amplitude along the phase coexistence with an ionic crystal that was recently found in Ref. [12].

The behavior of the charge-charge correlation function $h_D(x)$ depends on thermodynamic conditions. In Fig.1 a portion of the density-temperature phase diagram, as obtained in different theoretical [2, 3] and simulation [13] studies, is shown schematically. The solid lines represent boundaries of stability of the uniform fluid phase, and regions corresponding to different qualitative properties of $h_D(x)$ are separated by the dashed lines.

The Kirkwood line (K) separates the high-temperature/low-density region corresponding to an asymptotic monotonic decay of correlations, from the low-temperature/high-density region corresponding to exponentially damped oscillatory behavior of $h_D(x)$. In theories of the mean-field (MF) type the Kirkwood line is found to be a straight line $S = S_K = const$, where

$$S \equiv \frac{T^*}{\rho_0^*}. \quad (1)$$

In the above ρ_0^* is the dimensionless number-density (volume measured in σ^3 units, where σ

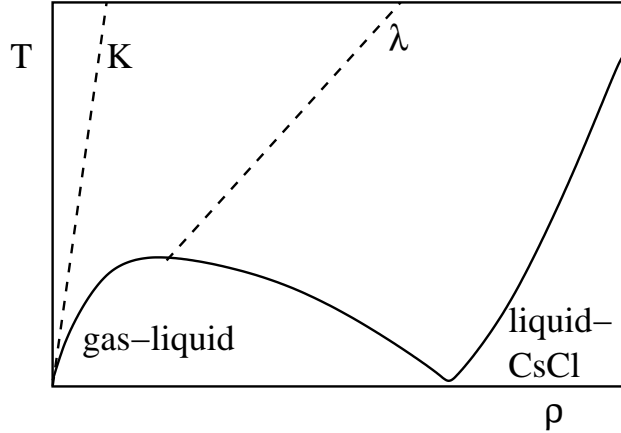


FIG. 1: A portion of the density-temperature phase diagram for the RPM as obtained in MF, shown schematically. Solid line separates the uniform fluid from the two-phase regions. Dashed lines denoted by 'K' and 'λ' represent the Kirkwood line and the λ-line respectively. T and ρ are in arbitrary units.

is the ion-diameter), and

$$T^* = \frac{D\sigma kT}{e^2} \quad (2)$$

is the temperature in standard reduced units (D is the dielectric constant of the solvent and e is the charge). In different theories the value of S_K is somewhat different, and typically $S_K \sim 10$. There is no controversy concerning this line, but there are no general reasons for this line to be straight beyond MF [3].

When the λ-line is approached from the high-temperature side, the decay length of correlations diverges [11, 14, 15]. The amplitude of the correlation function diverges [16] as well on the MF level of the field theory [11]. The low-temperature side of this line corresponds to a charge-ordered structure, where the nearest-neighbors (nn) are oppositely charged, and the λ-line represents a continuous transition between the uniform and the charge-ordered phases. The slope of this line shows a strong dependence on approximations and assumptions made in different theories [15]. In particular, in the MF approximation for the field theory the λ-line is $S = S_\lambda \approx 1.6$ [11], whereas the MSA yields $S_\lambda = 0$ [5]. The charge-ordered liquid phase was observed neither experimentally nor in simulations. A natural conclusion would be to question validity of theories that predict the existence of the λ-line. However,

the λ -line of continuous transitions to the charge-ordered phase was observed in simulations [17, 18, 19] of the lattice version of the RPM (LRPM), in agreement with predictions of the lattice version of the field theory [20]. Some other theories [21, 22, 23] yield for the LRPM similar results. The MSA, however, predicts an absence of such a transition in the LRPM. One might argue that the MSA theories are correct only in the continuum space, and the field theory yields correct results only on the lattice. This is indeed the case for the field theory in the MF approximation. Beyond MF, with the charge fluctuations accounted for in a Brazovskii-type approximation [12, 24, 25], the decay length of the charge-charge correlation function is found to be finite in the continuum-space RPM [12]. Thus, when the fluctuations are included in the field theory, there is no line of continuous transitions, in agreement with the MSA. At the same time the first-order transition to the ionic crystal is found [12] for the range of densities and temperatures that agree with simulations [13]. Thus, within the field theory we can calculate the correlation functions at the coexistence with the ionic crystal.

The field-theory results [12, 24, 25] also shed light on the nature of the λ -line that appears in MF. Beyond the Kirkwood line there is no qualitative change of the *average* structure of the liquid phase, which is represented by the correlation function. On the other hand, the line $S \approx 1.6$ separates the phase diagram (ρ_0^*, T^*) into two regions that correspond to different forms of the *most probable* instantaneous distributions of ions. At the high-temperature side of the line $S = S_\lambda$ the distribution of ions is most probably random. For $S < S_\lambda$, however, the most probable instantaneous distributions of the ions correspond to charge-density waves with a wavelength $\sim 2.5\sigma$, where σ is the hard-sphere diameter. According to the above prediction, in real-space representation charge-ordered clusters with a nn distance $\sim 1.27\sigma$ should dominate over randomly distributed ions for $S < S_\lambda$ in instantaneous charge distributions (i.e. in microscopic states). Such structures were indeed seen in simulation snapshots [26, 27]. In MF the average density distributions are approximated by the most probable distributions. When in a particular system the average- and the most-probable distributions agree on a qualitative level, the MF results are qualitatively correct. This is not the case in the RPM, therefore the line $S = S_\lambda$ is erroneously interpreted as a line of continuous phase transitions in MF theories. On the other hand, the occurrence of the λ -line on the MF level is an indication of the first-order transition to the ionic crystal, because beyond MF the first-order transition is found in the phase-space region where the

charge-ordered individual microstates are more probable than the microstates with randomly distributed ions.

In this work we focus mainly on the charge-charge correlations for $S < S_\lambda$, and calculate the number-number correlation function as well. In Ref.[16] the correlation functions are calculated within the field-theoretic description developed in Ref.[11] only in the Gaussian approximation. As already mentioned, at the λ -line the decay length and the amplitude of the charge-charge correlation function both diverge. Our purpose is to verify if the instantaneous order has some effect on the correlation functions beyond the Gaussian approximation. The results of Ref. [16] are extended beyond the Gaussian approximation within the Brazovskii theory [28]. It turns out that at the coexistence with the ionic crystal, obtained in Ref.[12], the amplitude and the decay length are quite small. Our results show that large decay length and amplitude of the charge-charge correlation function can be found only in the metastable liquid.

II. FORMALISM

A. Field-theoretic description of the RPM

In the field theory derived for the RPM in Ref.[11, 25, 29] the fluctuating fields are the local deviations from the most probable number- and charge densities, $\eta(\mathbf{x}) = \rho^*(\mathbf{x}) - \rho_0^* = \rho_+^*(\mathbf{x}) + \rho_-^*(\mathbf{x}) - \rho_0^*$ and $\phi(\mathbf{x}) = \rho_+^*(\mathbf{x}) - \rho_-^*(\mathbf{x})$ respectively. The most probable number density of ions is denoted by ρ_0^* , and the subscripts $+$ and $-$ refer to cations and anions respectively. Asterisks indicate that all densities are dimensionless (the unit volume is σ^3). ϕ is the charge density in e/σ^3 units. We focus on systems that are globally charge-neutral,

$$\int_{\mathbf{x}} \phi(\mathbf{x}) = 0, \quad (3)$$

where in this paper we use the notation $\int_{\mathbf{x}} \equiv \int d\mathbf{x}$. The fields $\eta(\mathbf{x})$ and $\phi(\mathbf{x})$ are thermally excited with the probability density [11, 25, 30]

$$p[\phi, \eta] = \Xi^{-1} \exp \left(-\beta \Delta \Omega^{MF}[\phi, \eta] \right), \quad (4)$$

where

$$\Xi = \int D\eta \int D\phi e^{-\beta \Delta \Omega^{MF}} \quad (5)$$

is the normalization constant and $\Delta\Omega^{MF}[\phi, \eta] = \Omega^{MF}[\phi, \rho^*] - \Omega^{MF}[0, \rho_0^*]$, where for $\phi = 0$ and $\rho^* = \rho_0^*$ the $\Omega^{MF}[\phi, \rho^*]$ assumes a minimum. In the theory studied in Refs. [11, 16, 25] Ω^{MF} is approximated by

$$\Omega^{MF}[\phi, \rho^*] = F_h[\phi, \rho^*] + U[\phi] - \mu \int_{\mathbf{x}} \rho(\mathbf{x}). \quad (6)$$

In the above μ is the chemical potential of the ions, $F_h[\phi, \rho^*] = \int_{\mathbf{x}} f_h(\phi(\mathbf{x}), \rho^*(\mathbf{x}))$ is the hard-core reference-system Helmholtz free-energy of the mixture in which the core-diameter σ of both components is the same. We use the Carnahan-Starling (CS) form of $f_h(\phi, \rho^*)$ in the local-density approximation, as in Ref.[12]. Finally, the energy in the RPM is given by

$$\beta U[\phi] = \frac{\beta^*}{2} \int_{\mathbf{x}} \int_{\mathbf{x}'} \frac{\theta(|\mathbf{x}' - \mathbf{x}| - 1)}{|\mathbf{x} - \mathbf{x}'|} \phi(\mathbf{x}) \phi(\mathbf{x}') = \frac{\beta^*}{2} \int_{\mathbf{k}} \tilde{\phi}(\mathbf{k}) \tilde{V}(k) \tilde{\phi}(-\mathbf{k}), \quad (7)$$

where $\int_{\mathbf{k}} \equiv \int d\mathbf{k}/(2\pi)^3$, and $\tilde{f}(\mathbf{k})$ denotes a Fourier transform of $f(\mathbf{x})$. Contributions to the electrostatic energy coming from overlapping cores are not included in (7). Here and below the distance is measured in σ units, and $\beta^* = 1/T^*$ with T^* defined in Eq.(2). The Fourier transform of $V(x) = \theta(x - 1)/x$, where $x = |\mathbf{x}|$, is

$$\tilde{V}(k) = 4\pi \cos k/k^2, \quad (8)$$

where k is in σ^{-1} units.

In the field theory the charge-density fields are considered. The correlation function for the fields at points \mathbf{x} and \mathbf{x}' , called the charge-density correlation function, is given by

$$G_{\phi\phi}(|\mathbf{x} - \mathbf{x}'|) \equiv \langle \phi(\mathbf{x}) \phi(\mathbf{x}') \rangle = \Xi^{-1} \int D\eta \int D\phi e^{-\beta\Delta\Omega^{MF}} \phi(\mathbf{x}) \phi(\mathbf{x}'). \quad (9)$$

The charge-density correlation function defined in Eq.(9) is related to the analog of the total charge-charge correlation function $h_D(x)$ [3, 5], and in Fourier representation this relation is given by

$$\frac{\tilde{G}_{\phi\phi}(k)}{\rho^*} = \tilde{h}_D(k) \rho^* + 1. \quad (10)$$

B. Weighted-field approximation

Because $\Delta\Omega^{MF}[0, \eta]$ is strictly local, the field η can be integrated out exactly [31] and Eq.(9) takes the form

$$G_{\phi\phi}(|\mathbf{x} - \mathbf{x}'|) = \Xi^{-1} \int D\phi e^{-\beta\mathcal{H}_{eff}[\phi]} \phi(\mathbf{x}) \phi(\mathbf{x}'), \quad (11)$$

where

$$\beta\mathcal{H}_{eff}[\phi] = \frac{1}{2} \int_{\mathbf{x}} \int_{\mathbf{x}'} \phi(\mathbf{x}) \mathcal{C}_{\phi\phi}^0(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}') + \sum_{m=2}^{\infty} \frac{\mathcal{A}_{2m}}{(2m)!} \int_{\mathbf{x}} \phi^{2m}(\mathbf{x}). \quad (12)$$

In the above

$$\mathcal{C}_{\phi\phi}^0(\mathbf{x}, \mathbf{x}') = C_{\phi\phi}^0(\mathbf{x}, \mathbf{x}') + f_2 \delta(\mathbf{x} - \mathbf{x}'), \quad (13)$$

where in Fourier representation $C_{\phi\phi}^0$ is given by

$$\tilde{C}_{\phi\phi}^0(k) = \frac{\delta\Delta\Omega^{MF}}{\delta\tilde{\phi}(\mathbf{k})\delta\tilde{\phi}(-\mathbf{k})}. \quad (14)$$

The f_2 and the coupling constants \mathcal{A}_{2m} are functions of ρ_0^* , whose exact forms depend on $f_h(\phi, \rho^*)$ [31], and have not been determined yet. Approximate expressions for \mathcal{A}_{2m} can be obtained in the weighted field approximation (WF) introduced in Ref.[11], and described in more detail in Refs. [25, 29, 30]. In the WF the field $\eta(\mathbf{x})$ is approximated by its most probable form for each given field $\phi(\mathbf{x})$. Another words, for a given field $\phi(\mathbf{x})$, the field $\eta(\mathbf{x})$ is determined by the minimum of $\beta\Delta\Omega^{MF}[\phi, \eta]$, i.e. it assumes the form

$$\eta_{WF}(\phi(\mathbf{x})) = \sum_n \frac{a_n}{n!} \phi(\mathbf{x})^{2n}, \quad (15)$$

where a_n are functions of ρ_0^* [12, 29]. The average density of ions in the WF is given by

$$\langle \rho^*(\mathbf{x}) \rangle = \rho_0^* + \Xi^{-1} \int D\phi e^{-\beta\mathcal{H}_{eff}[\phi]} \eta_{WF}(\phi(\mathbf{x})). \quad (16)$$

The WF approximation is equivalent to the lowest-order, zero-loop approximation for the exact $\mathcal{H}_{eff}[\phi]$ [31]. In the WF $f_2 = 0$ [31], and \mathcal{A}_{2n} and a_n , given in terms of derivatives of $f_h(\phi, \rho^*)$ at $\phi = 0$ and $\rho^* = \rho_0^*$, are functions of ρ_0^* [29].

In this work we limit ourselves to the ϕ^6 theory, with \mathcal{H}_{eff} approximated by

$$\beta\mathcal{H}_{WF}[\phi] = \frac{1}{2} \int_{\mathbf{x}} \int_{\mathbf{x}'} \phi(\mathbf{x}) \mathcal{C}_{\phi\phi}^0(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}') + \frac{\mathcal{A}_4}{4!} \int_{\mathbf{x}} \phi^4(\mathbf{x}) + \frac{\mathcal{A}_6}{6!} \int_{\mathbf{x}} \phi^6(\mathbf{x}). \quad (17)$$

The explicit forms of $\mathcal{A}_4(\rho_0^*)$ and $\mathcal{A}_6(\rho_0^*)$ in the WF theory with the CS approximation for f_h are given in Appendix A [12]. In the density interval $0.9 < \rho_0^* < 0.1541$ the above functional has to be supplemented with a term $\propto \phi^8$, to ensure stability of $\beta\mathcal{H}_{WF}[\phi]$ for $\phi \rightarrow \infty$. In this work we consider only $\rho_0^* > 0.1541$; for this range of densities $\mathcal{A}_6(\rho_0^*) > 0$. One should remember that the accuracy of the results obtained with the above functional depends on how large are the neglected contributions to $\beta\mathcal{H}_{eff}[\phi]$.

In the ϕ^6 theory the average density in the uniform phase, Eq.(16), is approximated by [12, 16]

$$\langle \rho^*(\mathbf{x}) \rangle = \rho_0^* + a_1 \langle \phi(\mathbf{x})^2 \rangle + \frac{a_2}{2!} \langle \phi(\mathbf{x})^4 \rangle, \quad (18)$$

where the explicit forms of $a_1(\rho_0^*)$ and $a_2(\rho_0^*)$, obtained in Ref. [12], are given in Appendix A. On the same level of approximation the number-density correlation function for $\mathbf{x} \neq \mathbf{x}'$ is given by

$$\begin{aligned} G_{\eta\eta}(\mathbf{x}, \mathbf{x}') &\equiv \langle \eta_{WF}(\mathbf{x}) \eta_{WF}(\mathbf{x}') \rangle^{con} = a_1^2 \langle \phi^2(\mathbf{x}) \phi^2(\mathbf{x}') \rangle^{con} \\ &+ \frac{a_1 a_2}{2} \left(\langle \phi^4(\mathbf{x}) \phi^2(\mathbf{x}') \rangle^{con} + (\mathbf{x} \leftrightarrow \mathbf{x}') \right) + \frac{a_2^2}{4} \langle \phi^4(\mathbf{x}) \phi^4(\mathbf{x}') \rangle^{con}, \end{aligned} \quad (19)$$

where

$$\langle f(\phi(\mathbf{x})) g(\phi(\mathbf{x}')) \rangle^{con} \equiv \langle f(\phi(\mathbf{x})) g(\phi(\mathbf{x}')) \rangle - \langle f(\phi(\mathbf{x})) \rangle \langle g(\phi(\mathbf{x}')) \rangle. \quad (20)$$

C. One-loop self-consistent Hartree approximation

Even for the approximate effective Hamiltonian (17), $G_{\phi\phi}$ given in Eq.(11) cannot be calculated analytically. In the perturbation theory [32, 33] $G_{\phi\phi}$ is given by Feynman diagrams [32, 33] with the $2n$ -point vertices \mathcal{A}_{2n} . The vertices at \mathbf{x} and \mathbf{x}' are connected by lines representing $G_{\phi\phi}^0(\mathbf{x} - \mathbf{x}')$, where G^0 is inverse to C^0 defined in Eq.(14), and all lines are paired. The corresponding expressions are integrated over all vertex points, or in Fourier representation over all $\tilde{G}_{\phi\phi}^0(k)$ -line loops, where [11, 12]

$$\tilde{G}_{\phi\phi}^{0-1}(k) = \tilde{C}_{\phi\phi}^0(k) = \beta^*(S + \tilde{V}(k)). \quad (21)$$

Note that

$$S = \frac{4\pi}{x_D^2}, \quad (22)$$

where

$$x_D = \kappa_D \sigma = \sqrt{4\pi\beta^* \rho_0^*} \quad (23)$$

is the dimensionless inverse Debye length.

The one-loop contribution to $\tilde{C}_{\phi\phi}$ (Fig.2a) is proportional to $\mathcal{A}_4 \mathcal{G}_0$, where

$$\mathcal{G}_0 = \int_{\mathbf{k}} \tilde{G}_{\phi\phi}^0(k). \quad (24)$$

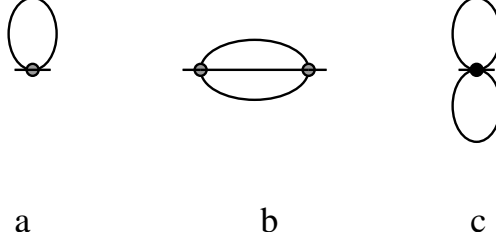


FIG. 2: Feynman diagrams contributing to $C_{\phi\phi}$ to two-loop order. The shaded circle and the bullet represent \mathcal{A}_4 and \mathcal{A}_6 respectively. Lines represent $G_{\phi\phi}^0$. In the self-consistent theory the lines represent $G_{\phi\phi}^H$.

Note that Eq.(21) can be written in the form

$$\tilde{C}_{\phi\phi}^0(k) = \beta^*(\tau_0 + \Delta\tilde{V}(k)) \quad (25)$$

where

$$\beta^*\tau_0 = \frac{1}{\rho_0^*} + \beta^*\tilde{V}(k_b), \quad (26)$$

$k = k_b$ corresponds to a minimum of $\tilde{V}(k)$, and

$$\Delta\tilde{V}(k) = \tilde{V}(k) - \tilde{V}(k_b) \simeq_{k \rightarrow k_b} v_2(k - k_b)^2 + O((k - k_b)^3). \quad (27)$$

The integrand in Eq.(24) diverges for $k = k_b$ when $\beta^*\tau_0 = 0$. For $k \rightarrow k_b$ Eq.(24) is of a similar form as the corresponding integral in the Brazovskii theory [28], and \mathcal{G}_0 diverges for $\beta^*\tau_0 \rightarrow 0$. In the effectively one-loop ϕ^6 theory (17), another contribution to $\tilde{C}_{\phi\phi}(k)$ is given by a diagram (Fig.2c) that is proportional to $\mathcal{A}_6\mathcal{G}_0^2$ [25, 29]. The symmetry factors of the graphs are calculated according to standard rules [32, 33].

In this work $\tilde{C}_{\phi\phi}$ is calculated in the effectively one-loop approximation, i.e. as in Ref.[12] the diagrams shown in Fig.2 a,c are taken into account. In the self-consistent, effectively one-loop Hartree approximation the inverse correlation function assumes the form [25, 28, 29]

$$\tilde{C}_{\phi\phi}^H(k) = r_0 + \beta^*\Delta\tilde{V}(k) \quad (28)$$

where

$$r_0 \equiv \tilde{C}_{\phi\phi}^H(k_b) = \beta^*\tau_0 + \frac{\mathcal{A}_4\mathcal{G}(r_0)}{2} + \frac{\mathcal{A}_6\mathcal{G}(r_0)^2}{8}, \quad (29)$$

and

$$\mathcal{G}(r_0) \equiv \langle \phi(\mathbf{x})^2 \rangle = \int_{\mathbf{k}} \tilde{G}_{\phi\phi}^H(k). \quad (30)$$

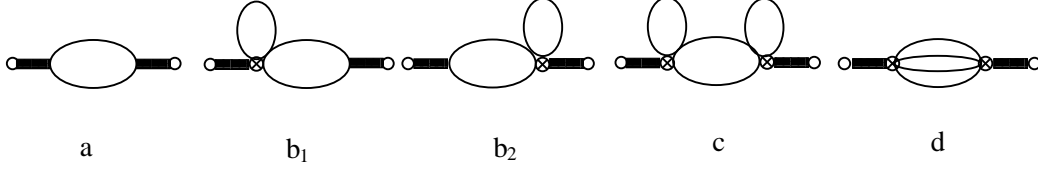


FIG. 3: Feynman diagrams contributing to $G_{\eta\eta}^H(\mathbf{x}_1, \mathbf{x}_2)$ given in Eq.(19). Open circles represent external points \mathbf{x}_1 and \mathbf{x}_2 . Lines connecting points \mathbf{x} and \mathbf{x}' represent $G_{\phi\phi}^H(\mathbf{x} - \mathbf{x}')$. The black box represents $1/\gamma_{0,2}$, the vertex from which the box and the two thin lines emanate represents $-\gamma_{2,1}$ and the circle with a cross inside represents $\Gamma_{4,1}^0$ (see Appendix A, Eqs.(47) and (51)). Symmetry factors are calculated according to standard rules [32, 33].

The integral (30) diverges because of the integrand behavior for $k \rightarrow \infty$. However, the contribution from $k \rightarrow \infty$ is unphysical (overlapping hard cores). When the fluctuations with $k \approx k_b$ dominate, which is the case for $r_0 \ll \beta^* v_2 k_b^2$, then the main physical contribution to $\mathcal{G}(r_0)$ comes from $k \approx k_b$. In this case

$$\tilde{C}_{\phi\phi}^H(k) \simeq r_0 + \beta^* v_2 (k - k_b)^2 \quad (31)$$

and the regularized integral is [28]

$$\mathcal{G}(r_0) = \int_{\mathbf{k}} \frac{1}{r_0 + \beta^* \Delta \tilde{V}(k)} \simeq_{r_0 \rightarrow 0} \int_{\mathbf{k}} \frac{1}{r_0 + \beta^* v_2 (k - k_b)^2} = \frac{2a\sqrt{T^*}}{\sqrt{r_0}}, \quad (32)$$

where

$$a = k_b^2 / (4\pi\sqrt{v_2}). \quad (33)$$

The self-consistent solution of the pair of equations (29) and (32) can be found analytically. The explicit expression for r_0 is given in Appendix B.

The above results allow for obtaining the number-density correlation function $G_{\eta\eta}$ at the same level of approximation. From Eq.(19) we obtain

$$G_{\eta\eta}^H(\mathbf{x}, \mathbf{x}') = \left(2a_1^2 + 12a_1 a_2 \mathcal{G}(r_0) + 18a_2^2 \mathcal{G}(r_0)^2 \right) G_{\phi\phi}^H(\mathbf{x}, \mathbf{x}')^2 + 3! a_2^2 G_{\phi\phi}^H(\mathbf{x}, \mathbf{x}')^4, \quad (34)$$

with the relevant diagrams shown in Fig.3, and the symmetry factors calculated according to standard rules [32, 33].

III. PROPERTIES OF THE CORRELATION FUNCTIONS

A. Gaussian approximation

In Ref.[16] the correlation function $G_{\phi\phi}$ was studied on the level of the Landau-type theory, where $G_{\phi\phi}$ is approximated by $G_{\phi\phi}^0$. In Fourier representation the above approximation for the charge-density correlation function is given in Eq.(21)[11, 16]. The Fourier transform $\tilde{G}_{\phi\phi}(k)$ of the correlation function defined in Eq.(11) reduces to $\tilde{G}_{\phi\phi}^0(k)$ given in Eq.(21) when all ϕ -dependent terms in $\beta\Delta\Omega^{MF}$, except from the Gaussian part $\frac{1}{2}\int_{\mathbf{k}}\tilde{\phi}(\mathbf{k})\tilde{C}_{\phi\phi}^0(k)\tilde{\phi}(-\mathbf{k})$, are neglected.

Let us first focus on the behavior of $\tilde{G}_{\phi\phi}^0(k)$ for $k \rightarrow 0$. From Eqs. (21) and (8) we obtain

$$\frac{\tilde{G}_{\phi\phi}^0(k)}{\rho_0^*} \simeq_{k \rightarrow 0} \frac{k^2}{k^2 + x_D^2}, \quad (35)$$

where the dimensionless Debye length x_D is given in Eq.(23). Note that Eq.(35) (with Eq. (10)) is consistent with the exact second-moment condition of Stillinger and Lovett [3, 4] and with the Debye-Hückel result.

For finite values of k the properties of $\tilde{G}_{\phi\phi}^0(k)$ agree with the results of other theories [15] only qualitatively [16]. The qualitative agreement with the GMSA results for $\tilde{h}_D(k)$ [5] is found only in the phase-space region given by

$$S \gg S_\lambda \equiv -\tilde{V}(k_b), \quad (36)$$

where S is defined in Eq.(1). The straight line $S = S_\lambda$ is equivalent to $\tau_0 = 0$, and represents the boundary of stability of the functional \mathcal{H}_{WF} in the (ρ_0^*, T^*) phase diagram [12, 25]. At this line the second functional-derivative of \mathcal{H}_{WF} vanishes for the most probable fluctuations [25, 34]. The line of instability of $\mathcal{H}_{WF}[\phi]$ is of course the same as the line of instability of the functional $\Delta\Omega^{MF}$ (see Eq.(14) and Refs.[12, 16, 25]). As shown in Ref. [16], the decay length and the amplitude of $G_{\phi\phi}^0(x)$ both diverge for $S \rightarrow S_\lambda$.

The charge-density correlation function in real-space representation is obtained in Ref.[16] by a pole analysis of $\tilde{G}_{\phi\phi}^0(k)$. The Kirkwood line in the Landau theory [16] is $S = S_K$, where

$$S_K = \frac{4\pi \cosh \alpha_K}{\alpha_K^2}, \quad \tanh \alpha_K = \frac{2}{\alpha_K}, \quad (37)$$

and $S_K \approx 11.8$. In the GMSA and in some other MF theories [5, 15] the Kirkwood line is also a straight line, but in the GMSA its slope was found to be $S_K = 4\pi/x_c^2 \approx 8.33$ [5]. For $S > S_K$ there are two inverse decay-lengths, a_1 and a_2 , and

$$xG_{\phi\phi}^0(x) = A_{\alpha\beta}^{(1)}e^{-a_1x} + A_{\alpha\beta}^{(2)}e^{-a_2x}. \quad (38)$$

For $S \rightarrow S_K^+$ the two imaginary poles of $\tilde{G}_{\phi\phi}^0(k)$, ia_1 and ia_2 , merge together and for $S < S_K$ a pair of conjugate complex poles, $i\alpha_0 \pm \alpha_1$, appears. As a result, $G_{\phi\phi}^0(x)$ exhibits an oscillatory behavior for $S < S_K$,

$$xG_{\phi\phi}^0(x) = -\mathcal{A}_{\phi\phi} \sin(\alpha_1 x + \theta) e^{-\alpha_0 x}, \quad (39)$$

with the amplitude $\mathcal{A}_{\phi\phi}$, the phase θ and the inverse lengths α_0 and α_1 given in Ref.[16]. When the λ -line is approached, both α_0 and $\mathcal{A}_{\phi\phi}$ diverge as $\propto (S - S_\lambda)^{-1/2}$, whereas $\theta \propto (S - S_\lambda)^{1/2}$ and $\alpha_1 \rightarrow k_b$.

The number-density correlation function in the above Landau theory for the RPM has the trivial form

$$G_{\eta\eta}^0 = \gamma_{0,2}^{-1} \delta(\mathbf{x} - \mathbf{x}'), \quad (40)$$

because the microscopic structure associated with hard spheres in the coarse-grained description is suppressed.

B. Charge-density correlation function in the self-consistent one-loop approximation

In this section we consider the charge-density correlation function (9) in the approximation outlined in sec.2.3. As already explained, our Brazovskii-type approximation relies on two important assumptions, and therefore it is valid only in a limited region of the phase diagram. In this section we determine the explicit form of the correlation functions and also the region of validity of our results. The approximate expression (28) for the inverse charge-density correlation function can be rewritten in the form

$$\tilde{C}_{\phi\phi}(k) = \left(S^H + \frac{4\pi \cos k}{k^2} \right) \beta^*. \quad (41)$$

This formula is analogous to Eq.(21) in Ref.[16], except that $S = T^*/\rho_0^*$ is replaced by

$$S^H = T^* r_0 - \tilde{V}(k_b). \quad (42)$$

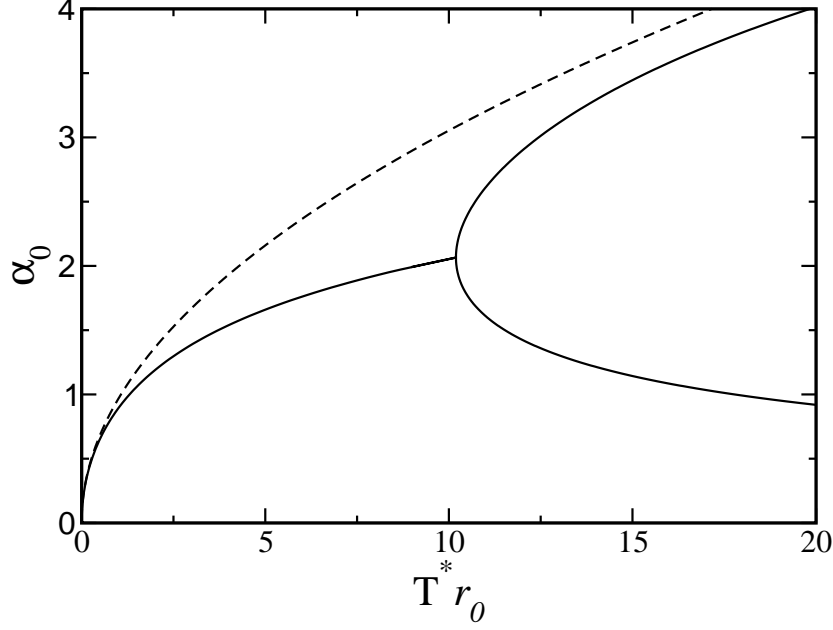


FIG. 4: The inverse decay length α_0 of the charge-density correlation function, as a function of $T^*r_0(\rho_0^*, T^*)$, where $r_0(\rho_0^*, T^*)$ is the self-consistent solution of Eqs.(29) and (32). For the explicit form of r_0 see Appendix B. The line $\alpha_0(T^*r_0)$ splits into two branches representing a_1 and a_2 at the Kirkwood line $T^*r_0 = S_K + \tilde{V}(k_b)$. Dashed line is the inverse decay-length obtained from the approximate form of $\tilde{C}_{\phi\phi}(k)$ (Eq.(31)).

The charge-density correlation function in real space can be obtained by following the pole analysis of Ref.[16], just by substituting S^H for S . The inverse lengths α_0 and α_1 are shown in Figs.4 and 5, where the numerical results obtained in Ref.[16] are used. Note that at the λ -line corresponding to the infinite range of correlations ($\alpha_0 = 0$), we find $T^*r_0 = 0$. From the explicit result for r_0 (Appendix B) it follows that $r_0 > 0$ for $T^* > 0$. For $T^* > 0$ the range of charge-density correlations is thus finite, in agreement with the results of the MSA and related approximations [3, 5], as well as with simulations.

The dashed line in Fig.4 represents α_0 for the approximate form of $\tilde{C}_{\phi\phi}(k)$ given in Eq.(31). The approximate form of \mathcal{G} , Eq.(32), and in turn the form of r_0 are based on the above approximation for $\tilde{C}_{\phi\phi}(k)$. As seen from Fig.4, Eq.(31) yields a good approximation for α_0 when $T^*r_0 \leq 1$ [12].

Note that the approximation for $\mathcal{G}(r_0)$ is valid only for $r_0 \ll \beta^*v_2k_b^2$. For $r_0 \gg \beta^*v_2k_b^2$ the fluctuations with wavenumbers other than $k \approx k_b$ give a relevant contribution to the integral in Eq.(30), and its value depends significantly on the regularization procedure. In

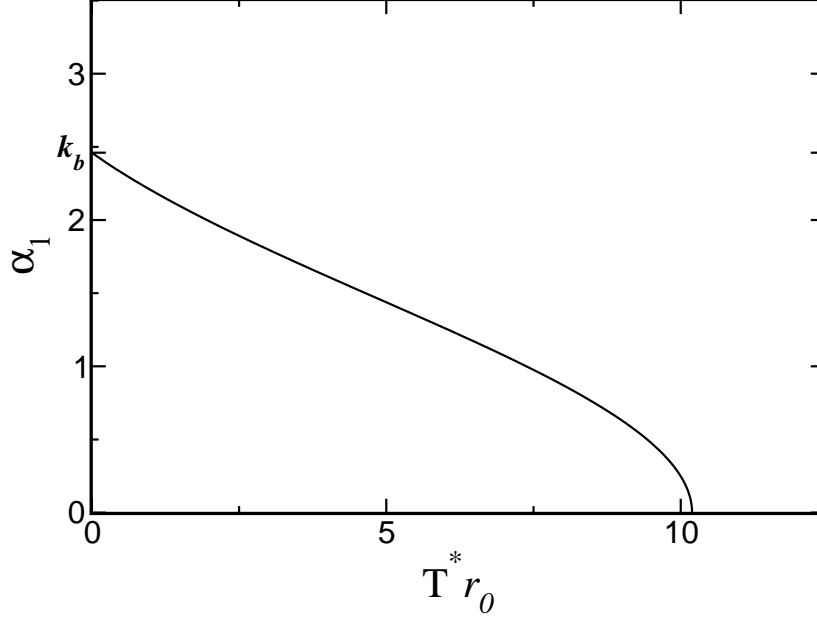


FIG. 5: $\alpha_1 = 2\pi/\lambda$, where λ is the period of damped oscillations of $G_{\phi\phi}(x)$, as a function of $T^*r_0(\rho_0^*, T^*)$, where $r_0(\rho_0^*, T^*)$ is the self-consistent solution of Eqs.(29) and (32), and its explicit form is given in Appendix B.

addition, in the Brazovskii ϕ^4 -theory the two-loop (Fig.2b) and higher-order diagrams can be neglected if $\mathcal{A}_4\sqrt{\beta^*v_2} \ll r_0$ [28]. From the two above conditions we obtain the region in the phase diagram,

$$T^* \ll \frac{v_2 k_b^4}{\mathcal{A}_4^2}, \quad (43)$$

where Eqs.(29) and (32) give accurate results in the field theory corresponding to the Hamiltonian (17). The line $T^* = v_2 k_b^4 / \mathcal{A}_4^2$ is shown in Fig.6 together with the coexistence line obtained in Ref.[12], and the K-line (44) discussed below. Note that the assumptions of our theory are satisfied near the phase coexistence for the high densities $\rho_0^* > 0.5$.

In the approximation derived in sec.3 the Kirkwood line is given by

$$S^H(\rho_0^*, T^*) = S_K \approx 11.8, \quad (44)$$

where S^H is given in Eq.(42), and the explicit expression for $r_0(\rho_0^*, T^*)$ is given in Appendix B. The line (44) is represented by the dotted line in Fig.6. Note that this line lies very far from the region of validity of the Brazovskii approximation. Note also that from Eq.(31) one obtains $\alpha_1 = k_b$. The approximation (31) fails of course when the Kirkwood line is approached, because at the Kirkwood line and beyond $\alpha_1 = 0$. We conclude that the

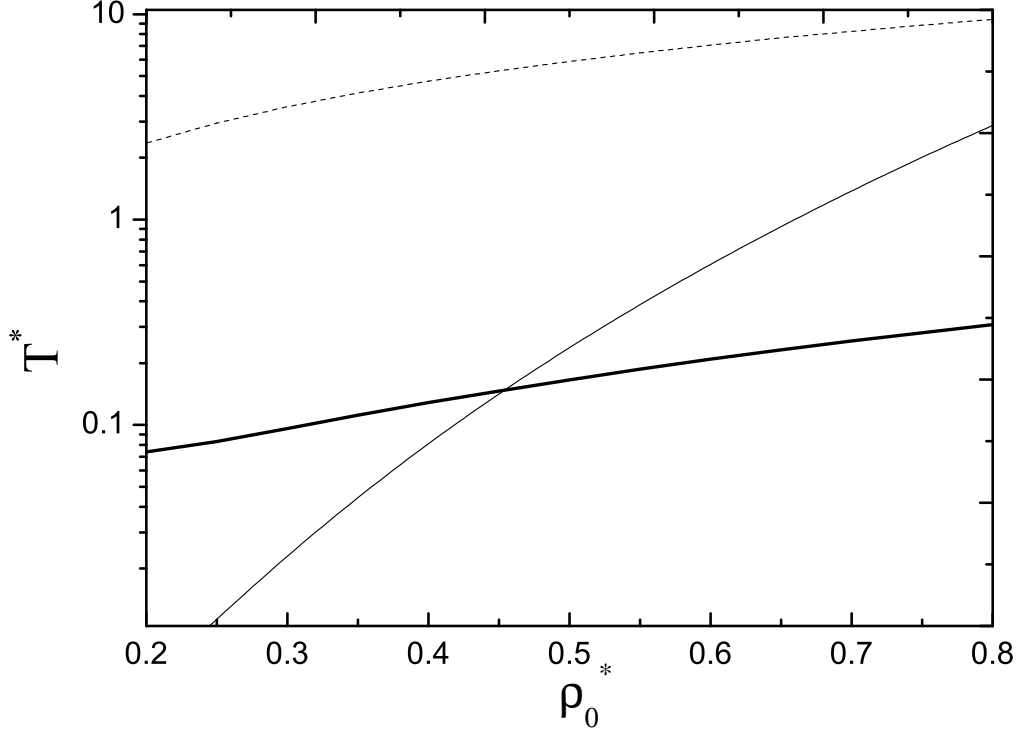


FIG. 6: Thin solid line represents $T^* = v_2 k_b^4 / \mathcal{A}_4^2$. For $T^* \ll v_2 k_b^4 / \mathcal{A}_4^2$ the results of the self-consistent one-loop approximation with (30) approximated by (32) are correct. In the rest of the phase diagram either the remaining Feynman diagrams (including the one shown in Fig.2b) have to be included, or the approximate form of $\mathcal{G}(r_0)$ (32) is not valid. Thick solid line represents the phase transition found in Ref.[12]. Dotted line is the Kirkwood line (44) in the self-consistent one-loop approximation.

assumptions of our version of the Brazovskii theory are satisfied near the phase coexistence for $\rho_0^* > 0.5$. When the K-line is approached, the theory becomes less accurate, and it fails completely beyond the K-line. On the other hand, beyond the K-line the simple Gaussian approximation yields results consistent with the exact predictions (see (35)).

C. Correlation functions at the coexistence with the ionic crystal

The transition between the liquid and ionic crystal was found in Ref.[12] in an approach consistent with the self-consistent one-loop approximation outlined in sec.2C. Note that

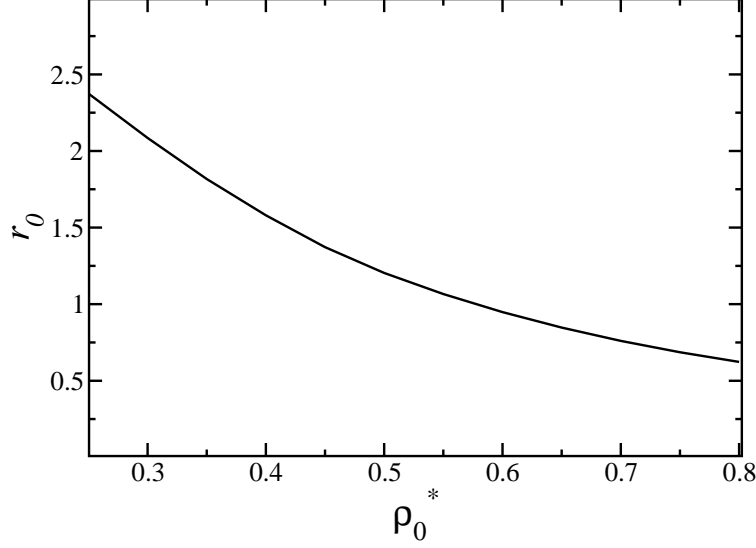


FIG. 7: $r_0(\rho_0^*)$ along the coexistence line $T^*(\rho_0^*)$ between liquid and the charge-ordered phase in the ϕ^6 -theory.

in the one-loop approximation $T^*\tilde{C}_{\phi\phi}(k)$ depends on the thermodynamic state through a single variable S^H . Since $\beta^*G_{\phi\phi}^H$ depends on the thermodynamic state only through $S^H = T^*r_0 + S_\lambda$ (Eq.(42)), we need to know T^*r_0 at the coexistence. From the explicit result for r_0 (Appendix B) and the result for the coexistence line $T^*(\rho_0^*)$ obtained in Ref.[12], we obtain $r_0(\rho_0^*)$ shown in Fig.7, and in turn we find $T^*r_0 \approx 0.2$ for $0.25 < \rho_0^* < 0.8$. The inverse lengths along the coexistence are thus nearly constant and independent of density, and their numerical values are found to be $\alpha_0 \approx 0.97$ and $\alpha_1 \approx 2.26$ on the basis of the results obtained in Ref.[16]. The approximate results for the amplitude and the phase are [16] $-\mathcal{A}_{\phi\phi} \approx 0.23S^H/\sqrt{S^H - S_\lambda} \approx 0.96$ and $\theta \approx 0.88\sqrt{S^H - S_\lambda} \approx 3.81$ respectively. The correlation functions along the phase coexistence are shown in Figs.8 and 9.

The inverse lengths α_0 and α_1 depend on the thermodynamic state through a single variable also in the MSA and related approximations [5], and $x_D = \kappa_D\sigma = \sqrt{4\pi/S}$ is usually chosen. Note that in our theory S^H reduces to S in MF; thus, the parameter $\sqrt{4\pi/S^H}$ reduces to x_D . At the transition $\sqrt{4\pi/S^H} \approx 2.25$. The characteristic inverse lengths in the GMSA for $x_D \approx 2.25$ can be read off from Fig.4 of Ref.[5], and they are $\alpha_0 \approx 1.5$ and $\alpha_1 \approx 2.1$. More precise values are given in Ref.[5] for $x_D = 4$, where $\alpha_0 = 1.32$ and $\alpha_1 = 2.89$, and for $x_D = 1.5$, where $\alpha_0 = 2.15$ and $\alpha_1 = 1.22$. Rather good agreement between the two theories is obtained, although in our theory the decay length is larger than

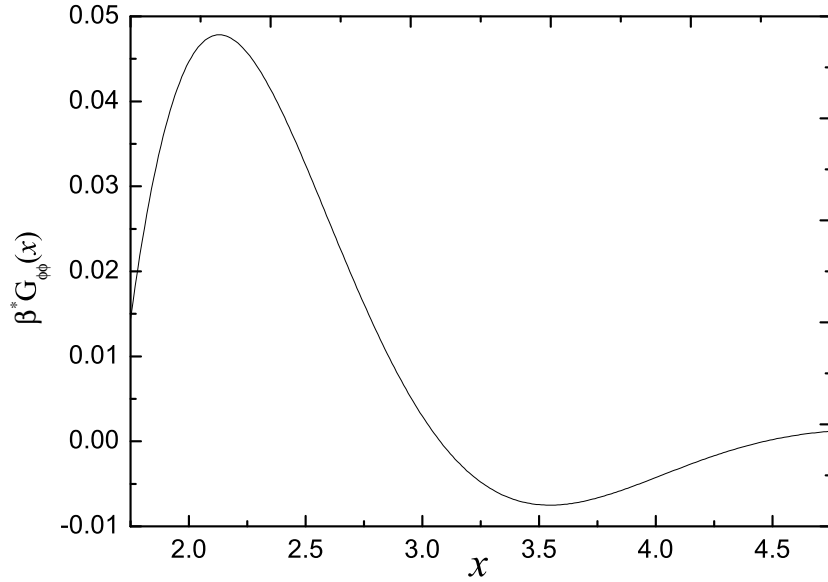


FIG. 8: Charge-density correlation function $\beta^* G_{\phi\phi}^H(x)$ in the liquid phase for $S^H \approx 1.8$ corresponding to the coexistence with the charge-ordered phase. $\beta^* G_{\phi\phi}^H(x)$ is dimensionless and x is in σ units.

in the GMSA. Similar fair agreement is obtained for the amplitude and the phase-shift.

Note that the form of $\beta^* G_{\phi\phi}^H(x)$ is the same along the phase coexistence, for a large range of density. This result is consistent with the structure of the ionic crystal coexisting with the liquid, where the nn distance is also independent of density on the same level of approximation. This result reflects the fact that the tendency for ordering in periodic structure follows directly from the form of the Coulomb potential.

The number-density correlation function is shown in Fig.9. In our theory the contribution to the correlation functions associated with hard-sphere ordering is neglected. The number-density correlation function shown in Fig.9 results from the coupling between the number- and the charge-density fluctuations, and is induced by the charge-ordering, which in turn follows from the form of the interaction potential. The exact form of the number-density correlation function should contain the entropic contribution due to the hard-spheres ordering, in addition to the interaction-induced contribution shown in Fig.9.

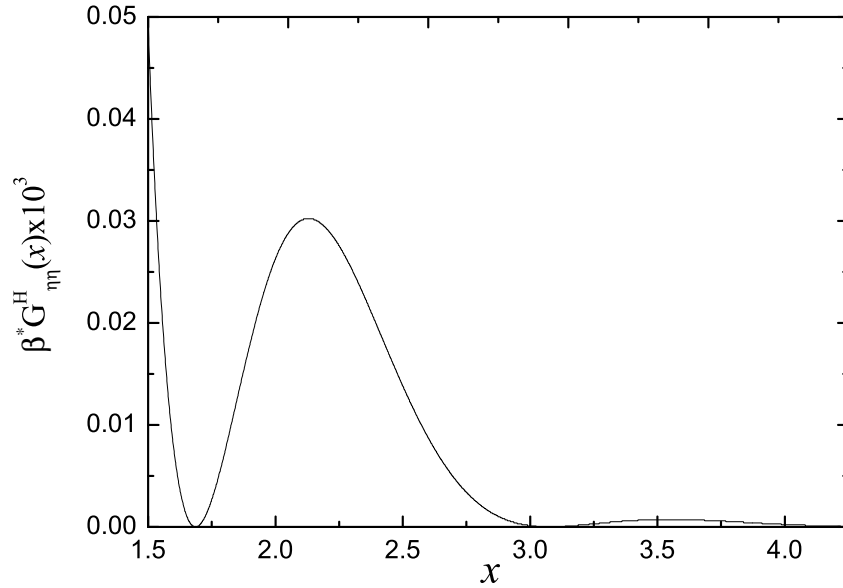


FIG. 9: Number-density correlation function $\beta^* G_{\eta\eta}^H(x)$ (Eq.(34)) in the liquid phase at coexistence with the charge-ordered phase for $\rho_0^* = 0.7$. Note that the number-density correlation function is three orders of magnitude smaller than the charge-density correlation function.

IV. SUMMARY

In this work the fluctuation contribution to the charge- and number-density correlation functions in the RPM is calculated within the Brazovskii-type theory. In MF the amplitude and the correlation length both diverge when the λ -line is approached. At the low-temperature side of the λ -line an instantaneous order occurs in the majority of the individual microscopic states, i.e. clusters with oppositely charged nn dominate over randomly distributed ions. Averaging over microscopic states with somewhat different order leads to a homogenization of the structure downhomogenization-induced first-order transition to the ionic crystal. Our purpose here was a verification if the instantaneous order found on the low- T side of the λ -line leaves some traces in the correlation functions. Our results show that the correlation length and the amplitude of $G_{\phi\phi}(x)$, both divergent in MF at the λ -line, show no indication of the MF singularity when the fluctuation contribution is included. Both quantities are of order of unity in the whole stability region of the fluid phase.

Acknowledgments

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V. APPENDICES

A. Coefficients $\mathcal{A}_4, \mathcal{A}_6, a_1$ and a_2 in the WF approximation

$$\mathcal{A}_4 = \gamma_{4,0} - 3 \frac{(-\gamma_{2,1})^2}{\gamma_{0,2}}, \quad (45)$$

$$\mathcal{A}_6 = \gamma_{6,0} - 15 \frac{(-\gamma_{2,1})(-\gamma_{4,1})}{\gamma_{0,2}} - 15 \frac{(-\gamma_{2,1})^3(-\gamma_{0,3})}{\gamma_{0,2}^3} - 45 \frac{(-\gamma_{2,2})(-\gamma_{2,1})^2}{\gamma_{0,2}^2}, \quad (46)$$

where

$$\gamma_{2m,n} = \frac{\partial^{2m+n} f_h(\phi, \rho)}{\partial \phi^{2m} \partial \rho^n} \Big|_{\phi=0, \rho=\rho_0^*}. \quad (47)$$

In the CS approximation they assume the explicit forms

$$\mathcal{A}_4 = -\frac{1 - 20s + 10s^2 - 4s^3 + s^4}{\rho_0^{*3}(1 + 4s + 4s^2 - 4s^3 + s^4)} \quad (48)$$

and

$$\mathcal{A}_6 = \frac{3W(s)}{\rho_0^{*5}(1 + 4s + 4s^2 - 4s^3 + s^4)^5}, \quad (49)$$

where

$$\begin{aligned} W(s) = & 3 - 84s + 360s^2 + 2644s^3 + 1701s^4 - 8736s^5 \\ & + 11240s^6 - 8304s^7 + 3861s^8 - 1164s^9 + 240s^{10} - 36s^{11} + 3s^{12}. \end{aligned}$$

The coefficients a_1 and a_2 in Eq.(18) are

$$a_1 = -\frac{\gamma_{2,1}}{2!\gamma_{0,2}}, \quad \frac{a_2}{2} = -\frac{\Gamma_{4,1}^0}{4!\gamma_{0,2}}. \quad (50)$$

where

$$\Gamma_{4,1}^0 = \gamma_{4,1} - \frac{6(-\gamma_{2,2})(-\gamma_{2,1})}{\gamma_{0,2}} - \frac{3(-\gamma_{3,0})(-\gamma_{2,1})^2}{\gamma_{0,2}^2}. \quad (51)$$

B. Explicit expression for r_0

By solving Eqs. (29) and (32) we obtain in the case of $\tau_0 < 0$ the explicit expression for r_0 ,

$$r_0 = \frac{1}{2} \left[\sqrt{u + v - p/3} + \sqrt{2(h - (u + v)/2 - p/3)} + \tau_0 \right], \quad (52)$$

where the following notations are introduced:

$$\begin{aligned} u &= \left(-b_2 + \sqrt{b_1^3 + b_2^2} \right)^{1/3}, & v &= \left(-b_2 - \sqrt{b_1^3 + b_2^2} \right)^{1/3}, \\ b_1 &= -\frac{1}{3} \left(\frac{p^2}{12} + 8a^2 T^* \mathcal{A}_4^2 \tau_0 \right), & b_2 &= \left(-\frac{p}{6} \right)^3 + \frac{4}{3} p a^2 T^* \mathcal{A}_4^2 \tau_0 - \frac{q}{2} \\ h &= \left[((u + v)/2 + p/3)^2 + 3(u - v)^2/4 \right]^{1/2} \\ p &= -(\tau_0^2 + 2a^2 T^* \mathcal{A}_6), \\ q &= a^4 T^{*2} \mathcal{A}_4^4. \end{aligned}$$

τ_0 and a are defined in Eqs.(26) and (33) respectively.

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